

AD-A285 224 INFORMATION PAGE Dist: A

Form Approved
OMB No. 0704-0188

See the average 1-hour per response, including the time for reviewing instructions, searching existing data sources, gathering the necessary information, and completing the report. Send comments regarding this burden estimate or any other aspect of this burden to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Pike, Office of Management and Budget, Paperwork Reduction Project (0704-0188), Washington, DC 20503.

1. AGENCY USE ONLY (Leave blank)		2. REPORT DATE		3. REPORT TYPE AND DATES COVERED ANNUAL 15 May 92 TO 14 May 93	
4. TITLE AND SUBTITLE EXCITED STATE CHEMISTRY OF PF, NF, AND NC1				5. FUNDING NUMBERS F49620-92-J-0275 63218C 1601/08	
6. AUTHOR(S) Dr D. W. Setser					
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Dept of Chemistry Kansas State University Willard Hall Manhattan KS 66506-3701				8. PERFORMING ORGANIZATION REPORT NUMBER AFOSR-TR-94 0613	
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) AFOSR/NL 110 Duncan Ave Suite B115 Bolling AFB DC 20332-0001 Dr. Berman				10. SPONSORING/MONITORING AGENCY REPORT NUMBER	
11. SUPPLEMENTARY NOTES 11 94-31487 					
12a. DISTRIBUTION/AVAILABILITY STATEMENT Approved for public release; distribution unlimited. A					
13. ABSTRACT (Maximum 200 words) The objective of our research program is to develop gas phase, chemically driven, energy storage systems that can serve as the media for short wavelength, electronic-transition lasers. We have selected the PF, AsF, and NF molecules for study, because of the success in the chemical generation and utilization of the excited singlet states of O2 in the oxygen-iodine laser. Our goals are to develop laboratory sources of the singlet states of PF and AsF and to characterize these states. We also wish to develop chemical sources of these molecules and then to utilize this stored energy, perhaps by energy-pooling reactions, to form a suitable upper laser state. Our laboratory already has considerable experience with the chemistry of the NF system. Unfortunately, NF(a) has not been successfully coupled to an acceptor state (other than perhaps I atoms) to build a laser. DTIC QUALITY INSPECTED 2					
14. SUBJECT TERMS				15. NUMBER OF PAGES	
				16. PRICE CODE	
17. SECURITY CLASSIFICATION OF REPORT (U)		18. SECURITY CLASSIFICATION OF THIS PAGE (U)		19. SECURITY CLASSIFICATION OF ABSTRACT (U)	
				20. LIMITATION OF ABSTRACT (U)	

Excited State Chemistry Of PF, NF AND NCl

Air Force Office Of Scientific Research (F49620-92-J-0275)

Annual Report (May, 92 - May, 93)

A. INTRODUCTION

The objective of our research program is to develop gas phase, chemically driven, energy storage systems that can serve as the media for short wavelength, electronic-transition lasers. We have selected the PF, AsF, and NF molecules for study, because of the success in the chemical generation and utilization of the excited singlet states of O₂ in the oxygen-iodine laser. Our goals are to develop laboratory sources of the singlet states of PF and AsF and to characterize these states. We also wish to develop chemical sources of these molecules and then to utilize this stored energy, perhaps by energy-pooling reactions, to form a suitable upper laser state. Our laboratory already has considerable experience with the chemistry of the NF system. Unfortunately, NF(a) has not been successfully coupled to an acceptor state (other than perhaps I atoms) to build a laser. All of the Group V diatomic halides molecules have the $\sigma^2\pi^4\pi^{*2}$ molecular orbital description for the lowest three electronic states, which are the $X^3\Sigma^-$, $a^1\Delta$ and $b^1\Sigma^+$ states in order of increasing energy. We currently are exploring the PF chemical system and we hope to begin work with the AsF molecule during the next 12 month period. The attractive feature of these two molecules and most other Group V diatomic halide molecules (except for NF and NCl) is the existence of a $A^3\Pi_{0,1,2}$ state that, in principle, can serve as an upper laser state. The energies of these states and sketches of the PF(X,a,b,A) molecular potentials are given in Figure 1. If the energy storage properties of the PF singlet states are satisfactory then coupling to a second chemical system to achieve energy extraction (which usually introduces numerous complications) possibly can be avoided. Even if the PF(a) and AsF(a) molecules can not be directly generated by chemical reactions, high concentrations can

ENERGY (ev)



$PF(d^1\Pi)$

$\tau = 1.0\mu s$

$PF(A^3\Pi)$

$\tau = 4.2\mu s$

$PF(b^1\Sigma^+)$

$\tau = 0.009s$

$PF(a^1\Delta)$

$\tau = 0.2-0.5s$

$PF(X^3\Sigma^-)$

$AsF(c^1\Pi)$

$AsF(A)$

τ (unknown)

$AsF(b)$

$\sim 0.001s$

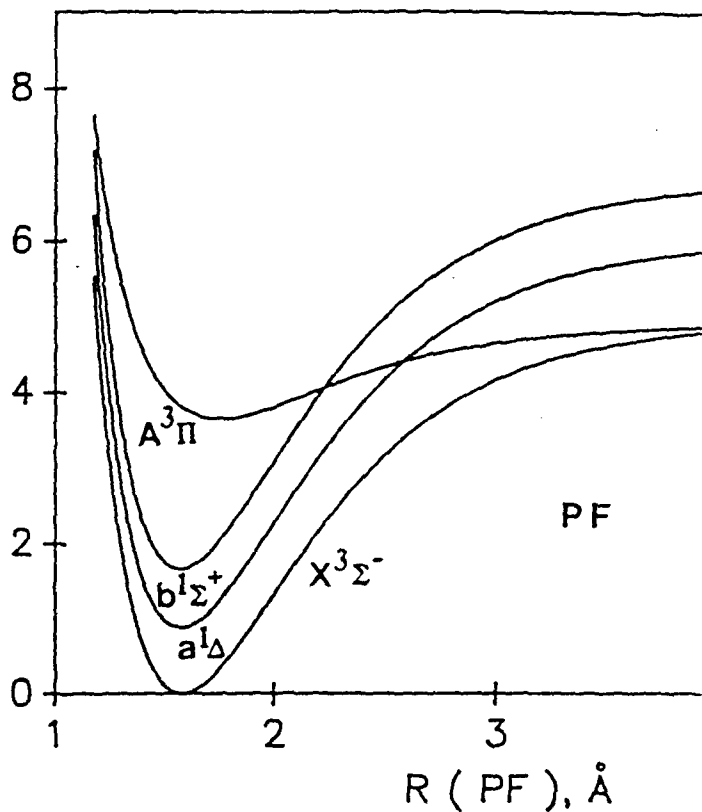
$AsF(a)$

τ (unknown)

$AsF(X)$

Figure 1

ENERGY (ev)



$NF(b)$

$\tau = 0.02s$

$NF(a)$

$\tau = 6s$

$NF(X)$

$O_2(b)$

$\tau = 12s$

$O_2(a)$

$\tau = 3900s$

$O_2(X)$

By
Distribution]

Availability Coeffs

Dist

Avail a of
Spec

A-1

be formed by energy transfer from $O_2(a)$ to the ground states. Thus, elucidation of the basic reaction chemistry of the AsF and PF systems seems to be very worthwhile. All experiments are done in discharge-flow reactors to isolate individual states, measure rate constants and identify products.

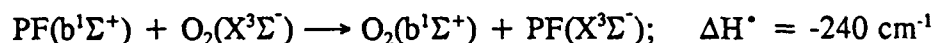
A long term goal of our research is to characterize energy-pooling reactions among the singlet metastable states of O_2 , NF, PF, AsF, etc. The energy of these singlet states is generally too low to be directly useful, and the energy from several molecules must be pooled in some way. For example, three or more molecules of $O_2(a)$ are required to produce the $I(^2P_{1/2})$ laser state in COIL. If we can develop chemical sources of PF(a) and AsF(a), or even better PF($b^1\Sigma^+$) and AsF($b^1\Sigma^+$), then the energy-pooling processes between the different a and b states offer interesting possibilities. Since these are second-order reactions, absolute concentrations are needed to obtain rate constants.

B. PROGRESS IN THE STUDY OF THE PF(a,b,A) STATES

Figure 1 gives a summary of the energies of the PF, AsF, NF and O_2 singlet states, plus the location of the $A^3\Pi_{0,1,2}$ states for PF and AsF. The PCl system has energy levels similar to those for PF. The $^1\Pi$ and $^3\Pi$ states arise by promoting an electron to the π^* antibonding orbital giving the $\sigma^1\pi^4\pi^3$ configuration. The presence of these $^3\Pi$ and $^1\Pi$ excited states is what makes LIF such a powerful analytical tool for monitoring the concentration of the lower states of AsF and PF. The radiative lifetimes of the $^1\Pi$ and $^3\Pi$ states are ~ 1 and $4 \mu s$, respectively, and they have long v'' progressions in their transitions to the lower states. We began our work with the PF system in May of 1992. Progress has been rapid because electrical discharges through dilute flows of He/PF₃ and Ar/PF₃ are rich sources of the PF(X,a,b) states, as well as PF₂(\bar{a}^4A_1). Preliminary experiments suggest that electrical discharges through flows of He/PCl₃ also provide entry into PCl chemistry. We also have started an investigation into ways of chemically generating PF($a^1\Delta$).

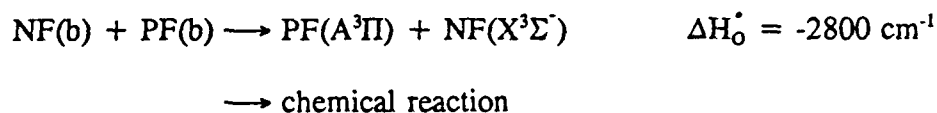
A low power dc discharge (~ 300 volts) in a dilute mixture of PF_3 in either He or Ar provides an adequate concentration ($\sim 10^9 \text{ cm}^{-3}$) of PF(b) to systematically study the quenching rate constants for $\text{PF(b}^1\Sigma^+)$. The relative concentration was monitored by the PF(b-X) transition, which has a radiative lifetime of 9.5 ms. The PF(b) molecules are readily quenched upon contact with the Pyrex glass wall of the reactor, but coating the walls with halocarbon wax provides an inert surface. Quenching constants have been measured for more than 20 reagents. The magnitudes of the rate constants are similar to those for the quenching of NF(b) . The rate constants generally are small and the pattern for the magnitudes of the rate constants implies that the mechanism is E-V transfer with concomitant formation of PF(a) . This tentative conclusion about the mechanism needs to be directly confirmed by measuring the growth of the PF(a) concentration, as the PF(b) concentration is quenched by added reagent, and this can be done by the LIF technique.

The quenching rate for PF(b) by added O_2 is relatively fast ($k_{\text{O}_2} = 2.1 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$) and from the weak $\text{O}_2(\text{b-X})$ emission we have identified $\text{O}_2(\text{b})$ as a product from the excitation-transfer reaction.



The reaction seems to be quantitative, but direct observation of PF(X) is desirable. This reaction can provide $\text{O}_2(\text{b})$ in a flow reactor in the absence of $\text{O}_2(\text{a})$, a rather rare situation.

The general lack of chemical reactivity of PF(b) (and also PCl(b)) is encouraging with respect to energy storage by the PF system. One of our next planned experiments is to study the interaction of PF(b) with NF(b) . The question to be answered is the ratio of the physical energy-pooling rate to the chemical reaction rate.



We have previously developed a source of NF(b) molecules, and we believe that the $[\text{NF(b)}]$ will

be high enough to study this important reaction under pseudo first-order conditions, i.e. $[NF(a)] > [PF(b)]$. This experiment has been delayed because of the lack of N_2F_4 in our laboratory. The valve on our old N_2F_4 tank failed, and the tank and contents could no longer be used. We currently are scheduled to receive another tank of N_2F_4 from the Aerospace Laboratory, when the tank arrives we will do the experiment.

During the course of our study of PF(b), we also have discovered and assigned the spectrum of the metastable $PF_2(\tilde{a}^4A_2)$ state. The dc discharge in a PF_3/He flow also generated this metastable radical.

A microwave discharge through a dilute PF_3/He flow provides an excellent source of $PF(X^3\Sigma^-)$ molecules that subsequently can be excited by a pulsed laser to selected vibrational levels of the $PF(A^3\Pi_{0,1,2})$ states. Very detailed, state specific relaxation processes in PF(A) can be studied. We have completed a comprehensive examination of the electronic state quenching of PF(A) by a series of molecular reagents and the vibrational and spin-orbit state relaxation in He and Ar. These data were acquired by observing the change in the pseudo first-order fluorescence decay constants of PF(A) with added reagent. These data (which were reported at the SPIE conference) provide the following points of view about the properties of PF(A) as a candidate for an upper laser state.

- (1) The radiative lifetime (4 μs) and the long progression in v'' is a positive factor.
- (2) The bond energy ($\geq 1 eV$) is adequate to prevent dissociation (or predissociation).
- (3) The stability toward electronic quenching by He and Ar is excellent.
- (4) The vibrational and spin-orbit relaxation rates are fast enough to enable the $PF(A, v')$ populations to reach Boltzmann conditions.
- (5) The quenching rate constants for most molecular reagents, other than perfluorinated molecules, tend to be larger than desirable.

Identification of the mechanism responsible for the electronic quenching of PF(A) remains as

a future goal. Since collision-induced predissociation is not possible, collisional transfer to a nearby PF^* metastable state or to $\text{PF}(b)$ is about the only viable alternative mechanism. Although there are no known states close in energy to $\text{PF}(A)$, molecular orbital considerations suggest that a $^3\Delta$ state could be in this energy region. An in-depth study of the rotational perturbations in the $\Omega = 0, 1, 2$ states of $\text{PF}(A^3\Pi)$ for a range of v' levels might provide some evidence about the location of a $\text{PF}(^3\Delta)$ or some other PF^* state.

The relaxation mechanism between the spin-orbit states seems to be complicated with transfer from $\Omega=2$ to $\Omega=0$ being faster than transfer $\Omega=2$ to $\Omega=1$. The relaxation scheme with preliminary assignments to the rate constants in He buffer are summarized below. The separation between the spin-orbit levels of $\text{PF}(^3\Pi)$ is $\sim 140 \text{ cm}^{-1}$

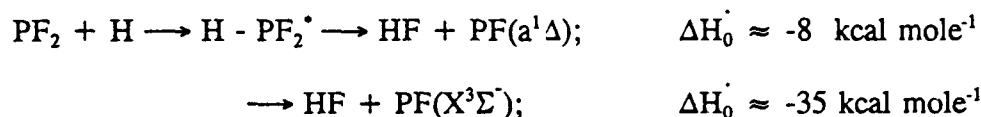


The magnitudes of the rate constants for the up-transition are set by detailed balance. The more facile collisional coupling between $\Omega=2$ and 0 rather than 2 and 1 is in accord with a theoretical prediction. However, the magnitudes and pattern for the spin-orbit relaxation rate constants are rather different from the isoelectronic $\text{SO}(A^3\Pi_{0,1,2})$ case. The vibrational relaxation from $\text{PF}(A, v'=1)$ is slower than spin-orbit state relaxation, so equilibration within the $v'=1$ spin-orbit states occurs before the population passes to $v'=0$. Very little quantitative data are available in the literature for spin-orbit relaxation processes. Comparison of the results for the SO, PF, PCl and AsF series of isoelectronic molecules should help elucidate the spin-orbit relaxation and electronic quenching mechanisms for these $^3\Pi_{0,1,2}$ states.

We began experiments to develop the LIF technique from $\text{PF}(a^1\Delta)$ using $\text{PF}(d^1\Pi)$ as the upper state in April. We found that the microwave discharge source for $\text{PF}(X)$, i.e., a

discharge through a dilute flow of PF_3/He , also provides an adequate concentration of $\text{PF}(a^1\Delta)$ for LIF detection. This welcome finding has several experimental implications. We can very easily measure the quenching constants of $\text{PF}(d^1\Pi)$ for comparison with the quenching constants of $\text{PF}(A^3\Pi)$. Furthermore, we can use the intensity of the LIF to monitor the relative concentration of $\text{PF}(a^1\Delta)$ for a fixed reaction time as a reagent is added to the reactor. The time integrated $\text{PF}(d \rightarrow a)$ fluorescence intensity is proportional to the total $[\text{PF}(a)]$ concentration and pseudo first-order decay constants can be measured. Thus, the chemistry of $\text{PF}(a)$ will be characterized during the summer months using LIF detection in our flow reactor. The reactions of $\text{PF}(X)$ with the same reagent can be examined in the same experiment by using the $A \leftarrow X$ transition to monitor the concentration of $\text{PF}(X)$. Such a comparison will help understand the differences between the reactivity of the singlet and triplet states of the $\sigma^2\pi^4\pi'^2$ configuration. Comparison of the $\text{PF}(a)$ rate constants with the published results for $\text{NF}(a)$ should be helpful. For energy storage applications, a chemically inert $\text{PF}(a)$ molecule is required.

We also have investigated a method for chemically producing the $\text{PF}(a^1\Delta)$ states. This effort was aided by Mr. C. Liu, a visitor from China. The plan was to use the $\text{H} + \text{PF}_2$ reaction, which by analogy to the $\text{H} + \text{NF}_2$ reaction, could generate $\text{PF}(a)$ with high efficiency. Mr. Liu synthesized PF_2Cl and PF_2Br because PF_3 does not react with H atoms at temperatures below 250 C. The anticipated reaction scheme is given below for excess H atoms.



Based upon the observed HF emission intensity and the HF vibrational distribution for short reaction times, the branching fraction for formation of $\text{PF}(a^1\Delta)$ must be less than 1.0 and the more exoergic triplet channel must have some importance. Using the LIF technique, both $\text{PF}(X)$ and $\text{PF}(a)$ have been directly observed in the reactor with $\text{PF}(a)$ showing the stronger LIF

interity. These results must be combined with the infrared chemiluminescence data and interpreted. Qualitative interpretations suggest that $[PF(X)] \ll [PF(a)]$. One of the main experimental difficulties has been gas handling for the PF_2Cl and PF_2Br molecules. Although the synthesis is straightforward and the sample can be stored at low temperature, there are unresolved, as yet, problems with regard to metering the desired pure quantities to the flow reactors from room temperature reservoirs containing mixtures of PF_2Cl or PF_2Br with He or Ar. Both molecules seem to react with glass storage reservoirs (stainless steel is worse) and further effort is needed to develop quantitative gas handling techniques. We seem to understand the $H + PF_2$ reaction better than the primary reactions of H atoms with PF_2Cl and PF_2Br .

The $H + PF_2$ reaction differs from $H + NF_2$ reaction because the weaker H-P bond and the stronger P-F bond changes the thermochemistry. Thus, formation of $PF(a)$ from $H + PF_2$ is only slightly exoergic. Since the PF and PF_2 thermochemistry is not well known, predicting specific products for given reactions is difficult. Nevertheless, the $H + PF_2$ reaction does have an appreciable branching fraction for generating $PF(a)$, and the analogy to the $H + NF_2$ reaction has some validity.

A second approach to chemically generating $PF(a)$ is to use the reaction of excess F atoms with PH_3 . The first step is known to be direct H abstraction to give FH_2 . In a preliminary experiment, we have observed strong $PF(b-X)$ emission early in the reaction chain. A possible explanation, which remains to be confirmed, is the following two reactions.



Another possibility is that $PF(b)$ was formed together with $PF(a)$.

C. PRELIMINARY RESULTS FOR $PCl(b)$ AND $NCI(b)$

Passing PCl_3/He or $NFCl_2/He$ flows through the low power dc discharge used to generate

PF(b) also gave useful concentrations for PCl(b) and NCl(b), respectively. The radiative lifetimes are sufficiently long that their kinetics can be studied in a fast flow reactor. Preliminary quenching data indicate that the pattern for the quenching constants will resemble that for PF(b). Since these (b) state molecules are not highly reactive, they are of general interest for energy storage and energy-pooling. Although our dc discharge source does not give high concentrations, it does provide a clean environment that permits lifetime and rate constant measurements. Such experiments will be done during the next year.

D. PROPOSED WORK WITH THE AsF CHEMICAL SYSTEM

We intend to initiate experiments with the AsF chemical system during the next year. Given the extensive literature on the spectroscopy of AsF from discharge sources, we are confident that our discharge apparatus with a dilute flow of AsF₃ in He or Ar will provide a useful source of AsF states for spectroscopic and kinetic studies. The spectroscopy of AsF is quite highly developed. Our first experiment will be to investigate the stability of AsF(A³Π_{0,1,2}) toward electronic quenching. The AsF(A³Π_{0,1,2}) states will be produced by pulsed laser excitation from AsF(X). Since D₀(AsF) > D₀(PF), but T_c(AsF(A)) < T_c(PF(A)); the AsF(A) state may be displaced enough that collisional quenching rates to other (unknown) AsF* states will be slower than for PF(A). If this expectation is found to be true, then we will engage in a comprehensive investigation of the chemistry of the AsF (a and b) states. An intriguing consequence of the AsF energetics shown in Figure 1 is that two AsF(b) molecules have enough energy to create AsF(A) by an energy-pooling reaction.

CUMULATIVE LISTING OF PUBLICATIONS

1. K. Du and D.W. Setser, "Quenching Constants of NF(a) by N₂F₄, NF₃, NF₂, NF(X), SiF₄, HNCO and NCO at 300K" J. Phys. Chem. In Press (1993).
2. S. Wategaonkar and D.W. Setser, "The F + HNCO Reaction System: A Flow Reactor

Source for HCO(X) and NF(X). J. Phys. Chem. In Press (1993).

3. J. Xu, D. Raybone and D.W. Setser "Radiative Lifetime and Quenching Constants of PF(A³Π)" SPIE Conference on Optics, Electro-Optics and Laser Applications to Science and Engineering, Jan (1993).
4. Y. Zhao and D.W. Setser "Generation of the PF₂(\tilde{a}^4A_2) Radical and Assignment of the PF₂($\tilde{a}-\tilde{X}$) Emission Spectrum". Chem. Phys. Lett. In Press (1993).
5. E. Arunan, C.P. Liu, D.W. Setser, J.V. Gilbert and R.D. Coombe, "Infrared Chemiluminescence Studies of the H + NCl₂ and H + NFCl Reactions", J. Phys. Chem. submitted (1993).
6. Y. Zhao and D.W. Setser, "Generation of the PF(b¹Σ⁺) Molecule and Characterization of the Lifetime and Quenching Constants" J. Phys. Chem. to be submitted (1993).